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(54) **METHOD FOR COLLECTION OF VALUABLE METAL FROM ITO SCRAP**

(57) Proposed is a method for collecting valuable metal from an ITO scrap including the steps of subjecting the ITO scrap to electrolysis in pH-adjusted electrolyte, and collecting indium or tin as oxides. Additionally proposed is a method for collecting valuable metal from an ITO scrap including the steps of subjecting the ITO scrap to electrolysis in an electrolytic bath partitioned with a diaphragm or an ion-exchange membrane to precipitate hydroxide of tin, thereafter extracting anolyte temporarily, and precipitating and collecting indium contained in the

anolyte as hydroxide. With the methods for collecting valuable metal from an ITO scrap described above, indium or tin may be collected as oxides by roasting the precipitate containing indium or tin. Consequently, provided is a method for efficiently collecting indium from an ITO scrap of an indium-tin oxide (ITO) sputtering target or an ITO scrap such as ITO mill ends arisen during the manufacture of such ITO sputtering target.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a method for collecting valuable metal from an ITO scrap such as a spent indium-tin oxide (ITO) sputtering target or ITO mill ends arisen during the manufacture of the ITO sputtering target (hereinafter collectively referred to as an "ITO scrap" in this specification).

BACKGROUND ART

[0002] In recent years, an indium-tin oxide ($\text{In}_2\text{O}_3\text{-SnO}_2$; generally known as ITO) sputtering target is being widely used for a transparent conductive thin film of an LCD device or a gas sensor. In many cases, however, a thin film is formed on a substrate or the like by employing the sputtering method as the thin-film forming means.

[0003] Although the sputtering method as the thin-film forming means is a superior method, if a sputtering target is used to form a transparent conductive thin film, the target will not be consumed uniformly. A portion of the target with severe consumption is generally referred to as an eroded portion, and the sputtering operation is continued until immediately before a backing plate supporting the target becomes exposed due to the further consumption of the eroded portion. This target is subsequently replaced with a new target.

[0004] Accordingly, a spent sputtering target will have numerous non-eroded portions; that is, unused portions of the target, and all of these portions become scrap. Moreover, even during the manufacture of ITO sputtering targets, scraps (mill ends) will arise from grinding dust and cutting wastage. Generally speaking, the scrap contains roughly 9.7wt% of tin oxide (SnO_2), but the scrap is mostly indium oxide (In_2O_3).

[0005] Because high-purity materials are used as the ITO sputtering target material and because indium is particularly expensive, indium and tin are simultaneously collected from the foregoing scrap materials. As this kind of indium collection method, conventionally, a method that combines wet refining such as the acid solution process, ion exchange method, and solvent extraction method is used.

[0006] For instance, there is a method of subjecting an ITO scrap to cleansing and pulverization, dissolving the ITO scrap in nitric acid, precipitating and eliminating impurities, such as zinc, tin, lead and copper, as sulfide by passing hydrogen sulfide through the solution, thereafter adding ammonia to neutralize the solution, and collecting the resulting indium hydroxide.

[0007] Nevertheless, the indium hydroxide obtained by the foregoing method has inferior filtration property, requires long operational process, and contains large amounts of impurities such as Si and Al. In addition, with the created indium hydroxide, since the grain size and

grain size distribution will vary depending on the neutralization condition, maturation condition and other conditions, there is a problem in that the characteristics of the ITO target cannot be stably maintained upon subsequently manufacturing such ITO target.

[0008] Conventional technology and its advantages and disadvantages are described below.

[0009] As one example of such conventional technology, there is an etching method of a transparent conductive film including the steps of reducing an ITO film deposited on a substrate by an electrochemical reaction in the electrolyte, and dissolving the reduced transparent conductive film in the electrolyte (refer to Patent Document 1). However, the object of this method is to obtain a mask pattern with high precision, and relates to technology that is different from the collection method.

[0010] For pretreatment to collect valuable metal from ITO, there is also technology of separating, in the electrolyte, the impurities contained in an In-based brazing filler material used in the bonding with the backing plate (refer to Patent Document 2). Nevertheless, this method does not relate to technology of directly collecting valuable metal from ITO.

[0011] Moreover, upon collecting indium from an intermediate obtained as a byproduct of the zinc refining process or an ITO scrap, disclosed is technology of separating tin as halogenated stannate, performing reduction treatment with hydrochloric acid or nitric acid solution, subsequently adjusting the pH of this aqueous solution to 2 to 5, reducing metallic ions of iron, zinc, copper, thallium and the like in order to make the metallic ions into a substance that will not precipitate easily, and separating the indium component in the aqueous solution (refer to Patent Document 3). With this technology, however, there is a problem in that the refining process is complicated, and a superior refining effect cannot be expected.

[0012] Further, as a method for collecting high-purity indium, disclosed is technology of dissolving ITO in hydrochloric acid, adding alkali thereto to make the pH 0.5 to 4, eliminating tin as hydroxide, subsequently blowing hydrogen sulfide gas in order to eliminate hazardous materials such as copper and lead as sulfide, and electrowinning indium metal by performing electrolysis using the obtained solution (refer to Patent Document 4). There is a problem with this technology in that the refining process is complicated.

[0013] In addition, proposed is a method of dissolving an ITO indium-containing scrap in hydrochloric acid to obtain an indium chloride solution, adding a sodium hydroxide solution to this solution to eliminate tin as tin hydroxide, additionally adding a sodium hydroxide solution after the elimination to obtain indium hydroxide, filtering the obtained indium hydroxide to obtain indium sulfate from the filtered indium hydroxide, and obtaining indium by electrowinning the indium sulfate (refer to Patent Document 5). Although this is an effective method with a significant refining effect, there is a drawback in that the process is complicated.

[0014] Also proposed is a method for collecting indium including the steps of dissolving an ITO indium-containing scrap in hydrochloric acid to obtain an indium chloride solution, adding a sodium hydroxide solution to the indium chloride solution to eliminate tin contained in the scrap as tin hydroxide, substituting indium with zinc from the solution after eliminating the tin hydroxide, and thereafter collecting indium (refer to Patent Document 6). Although this is also an effective method with a significant refining effect, there is a drawback in that the process is complicated.

[0015] Additionally disclosed is a method for collecting metallic indium including the steps of extracting suboxide-containing cast scrap floating on molten metallic indium, introducing this into an atmosphere furnace, introducing argon gas into the furnace after evacuating the furnace once, heating the furnace to a prescribed temperature, and reducing the suboxide-containing cast scrap (refer to Patent Document 7).

[0016] Although this is in itself an effective method, there is a drawback in that this is not a fundamental collection method of ITO scrap.

[0017] In light of the above, a method that is efficient and with a versatile collection process is being sought.

[Patent Document 1] Japanese Patent Laid-Open Publication No. S62-290900

[Patent Document 2] Japanese Patent Laid-Open Publication No. H8-41560

[Patent Document 3] Japanese Patent Laid-Open Publication No. H3-82720

[Patent Document 4] Japanese Patent Laid-Open Publication No. 2000-169991

[Patent Document 5] Japanese Patent Laid-Open Publication No. 2002-69684

[Patent Document 6] Japanese Patent Laid-Open Publication No. 2002-69544

[Patent Document 7] Japanese Patent Laid-Open Publication No. 2002-241865

DISCLOSURE OF THE INVENTION

[0018] In order to overcome the foregoing problems, the present invention provides a method for efficiently collecting indium and tin as oxides from an ITO scrap of an indium-tin oxide (ITO) sputtering target or an ITO scrap such as ITO mill ends arising during the manufacture of such ITO sputtering target.

[0019] Thus, the present invention provides a method for collecting valuable metal from an ITO scrap including the steps of subjecting the ITO scrap to electrolysis in pH-adjusted electrolyte, and collecting indium and tin as oxides.

[0020] As the electrolyte upon collecting valuable metal from the ITO scrap, sulfuric acid solution, hydrochloric acid solution, nitric acid solution or the like is primarily used. The foregoing electrolyte solutions are preferable examples and there is no particular limitation on the elec-

trolyte solution that may be used. And, the conditions for efficiently collecting valuable metal may be arbitrarily selected. The foregoing are preferable examples for precipitating tin as tin hydroxide, and further collecting indium as hydroxide.

[0021] The conditions including the current density for performing electrolysis to the scrap such as mill ends are not uniformly defined, and the current density is appropriately selected according to the amount of such mill ends or the property of the material. The liquid temperature of the electrolyte solution is generally in the range of 0 to 100°C, and preferably in the range of 20 to 50°C.

[0022] The method for collecting indium by electrolysis according to the present invention is an extremely simple method since the ITO scrap is simply subject to electrolysis as an anode. Nevertheless, no conventional technology has previously adopted this kind of method. The collected indium can be used for the recycle of an ITO sintered target.

[0023] The provided method for efficiently collecting indium hydroxide and tin oxide is a superior method in which indium oxide and tin oxide can be collected extremely easily; that is, an ITO scrap of an indium-tin oxide (ITO) sputtering target or an ITO scrap such as ITO mill ends arising during the manufacture of such ITO sputtering target is simply subject to electrolysis as an anode.

BEST MODE FOR CARRYING OUT THE INVENTION

[0024] The present invention provides a method for precipitating and efficiently collecting tin or indium as hydroxide from scraps containing indium and tin of an ITO target by electrolysis.

[0025] As the electrolyte, an acid solution of sulfuric acid, hydrochloric acid, nitric acid or the like may be used. Moreover, in order to improve the current efficiency, well-known additive agents may also be used. The use of an additive agent is subject to the condition that such additive agent will not deteriorate the purity of the product.

[0026] As described above, if indium can be collected, it should be understood that a recycled ITO can also be manufactured easily.

[0027] A special electrolytic apparatus is not required. For instance, the ITO to be subject to electrolysis is used as the anode, and a corrosion-resisting electrode such as carbon is used as the cathode mother plate when performing electrolysis. It is thereby possible to avoid the increase or inclusion of impurities in the anode.

[0028] It is desirable to adjust the current density as needed based on the type of raw material. The factor to be adjusted in this case is only the production efficiency. Although there is no particular limitation on the electrolysis temperature, desirably electrolysis is performed by adjusting the temperature to be in a range of 0 to 100°C. Since the current efficiency will deteriorate if the electrolysis temperature is less than 0°C and the evaporation of the electrolyte will increase if the electrolysis temperature exceeds 100°C, a more preferable range of the electrol-

ysis temperature is 20 to 50°C.

[Examples]

[0029] The present invention is now explained in detail with reference to the Examples. These Examples are merely illustrative, and the present invention shall in no way be limited thereby. In other words, various modifications and other embodiments based on the technical spirit claimed in the claims shall be included in the present invention as a matter of course.

(Example 1)

[0030] 2kg of ITO (indium oxide-tin oxide) scrap was used as the raw material. The components in this raw material were 9.7wt% of tin oxide (SnO_2) and the remainder indium oxide (In_2O_3).

[0031] The raw material was placed in an anode box, and electrolysis was performed in a sulfuric acid solution of pH2 at a liquid temperature of 50°C. Consequently, tin precipitated as hydroxide. It was thereby possible to obtain hydroxide of Sn from the ITO (indium oxide-tin oxide) scrap. Moreover, Sn oxide was obtained by roasting the hydroxide. The oxide obtained by this method was approximately 0.18kg. Incidentally, In electrodeposited on the cathode side as metal.

(Example 2)

[0032] 2kg of ITO (indium oxide-tin oxide) scrap was used as the raw material. The components in this raw material were 9.7wt% of tin oxide (SnO_2) and the remainder indium oxide (In_2O_3).

[0033] The raw material was placed in an anode box, and electrolysis was performed in a 3N hydrochloric acid solution at a liquid temperature of 50°C. The solution containing the dissolved indium and tin was extracted, pH was set to 1, and tin was precipitated and eliminated as hydroxide. The anode and the cathode were partitioned with a diaphragm. An anion-exchange membrane may also be used in substitute for the diaphragm.

[0034] The In-containing solution, from which tin was eliminated, was placed in a cathode box, and electrolysis was performed in a sulfuric acid solution of pH6. It was thereby possible to collect hydroxide of In from the ITO (indium oxide-tin oxide) scrap. The indium obtained by this method was approximately 1.8kg. Moreover, it was also possible to collect tin as hydroxide.

(Example 3)

[0035] 2kg of ITO (indium oxide-tin oxide) scrap was used as the raw material. The components in this raw material were 9.7wt% of tin oxide (SnO_2) and the remainder indium oxide (In_2O_3).

[0036] The raw material was placed in an anode box, and electrolysis was performed in a 1N nitric acid solution

at a liquid temperature of 30°C. Consequently, tin precipitated as metastannic acid. The remaining solution was extracted and neutralized with pH8 to obtain indium hydroxide. The obtained indium hydroxide was roasted to obtain an oxide. It was thereby possible to obtain approximately 0.19kg of tin oxide and approximately 1.75kg of indium oxide.

(Example 4)

[0037] 2kg of ITO (indium oxide-tin oxide) scrap was used as the raw material. The components in this raw material were 9.7wt% of tin oxide (SnO_2) and the remainder indium oxide (In_2O_3).

[0038] The raw material was placed in an anode box, and electrolysis was performed in a 3N sulfuric acid solution at a liquid temperature of 20°C. The Sn^{2+} that dissolved in the sulfuric acid solution was subject to air bubbling. Consequently, tin precipitated as hydroxide. In this case, the same result was obtained even when an oxidizing agent (for instance, H_2O_2) was placed therein.

[0039] The dissolved solution was extracted and neutralized with sodium hydroxide to precipitate indium as hydroxide. The foregoing hydroxides were respectively roasted to obtain oxides. It was thereby possible to separately collect indium oxide and tin oxide from the ITO (indium oxide-tin oxide) scrap. Approximately 0.18kg of tin oxide and approximately 1.7kg of indium oxide were obtained.

[0040] Although in each of the foregoing Examples, ITO (indium oxide-tin oxide) mill ends or ITO scraps containing 9.7wt% of tin oxide (SnO_2) and remainder indium oxide (In_2O_3) were used, it is possible to arbitrarily change the electrolytic conditions such as the current density and pH according to the component amount of In_2O_3 and SnO_2 , and it goes without saying that there is no particular limitation on the component amount of the raw material. In particular, although the content of tin oxide (SnO_2) in the ITO is changed between 5wt% to 30wt%, the present invention can still be applied to this case.

[0041] In addition, although there are cases where small amounts of accessory components are added to the ITO, so as long as ITO is the basic constituent, it goes without saying that the present invention can also be applied to this case.

INDUSTRIAL APPLICABILITY

[0042] The present invention yields a significant industrial advantage in terms of recycling of the expensive indium, since provided is a superior method in which indium or tin can be collected as oxides extremely easily and efficiently; that is, an ITO scrap of an indium-tin oxide (ITO) sputtering target or an ITO scrap such as ITO mill ends arising during the manufacture of such ITO sputtering target is simply subject to electrolysis as an anode.

Claims

1. A method for collecting valuable metal from an ITO scrap including the steps of subjecting the ITO scrap to electrolysis in pH-adjusted electrolyte, and collecting indium or tin as oxides. 5
2. A method for collecting valuable metal from an ITO scrap including the steps of subjecting the ITO scrap to electrolysis in an electrolytic bath partitioned with a diaphragm or an ion-exchange membrane to precipitate hydroxide of tin, thereafter extracting anolyte temporarily, and precipitating and collecting indium contained in the anolyte as hydroxide. 10
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3. The method for collecting valuable metal from an ITO scrap according to claim 1 or claim 2, wherein indium or tin is collected as oxides by roasting the precipitate containing indium or tin. 20
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2007/062897

A. CLASSIFICATION OF SUBJECT MATTER <i>C25B1/00(2006.01)i, C22B3/44(2006.01)i, C22B25/06(2006.01)i, C25C1/14(2006.01)i, C25C1/22(2006.01)i</i> According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) <i>C25B1/00, C22B3/44, C22B25/06, C25C1/14, C25C1/22</i> Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched <i>Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2007</i> <i>Kokai Jitsuyo Shinan Koho 1971-2007 Toroku Jitsuyo Shinan Koho 1994-2007</i> Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2003-247089 A (Nikko Materials Co., Ltd.),	1, 2
Y	05 September, 2003 (05.09.03), Full text (Family: none)	3
Y	JP 2005-314786 A (Mitsui Mining & Smelting Co., Ltd.), 10 November, 2005 (10.11.05), Par. No. [0034] & WO 2005/095659 A1	3
☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
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Date of the actual completion of the international search 18 September, 2007 (18.09.07)		Date of mailing of the international search report 02 October, 2007 (02.10.07)
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REFERENCES CITED IN THE DESCRIPTION

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